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DEVELOPMENT OF A METHOD FOR CLEANING
FLEXIBLE STAINLESS STEEL LINES

National Aeronautics and Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama

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ABSTRACT

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A method is described for removing the outermost layers of metal from flexible metal components used in booster vehicle fuel and oxygen lines. While "pickling," "bright-dipping," "passivating," and similar treatments used for stainless alloys can be applied readily to small parts, this type of treatment for very large (2 and 3 ft diameter) ducts is physically impractical. The new method employs a mild electrolyte--20% sodium chloride, for example--applied to the metal surface through a metal jet. A DC voltage is applied between the jet and the workpiece (the latter being positive) so that continuous dissolution occurs where the electrolyte jet strikes. The stream is played on the surface with a sweeping motion, allowing reasonably uniform current distribution and controlled "deplating" of the surface.

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DEVELOPMENT OF A METHOD FOR CLEANING
FLEXIBLE STAINLESS STEEL LINES

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The fact that the components in question must be stored under various conditions of temperature and humidity--not to mention eventual exposure to a seacoast atmosphere at the launching site, perhaps for months--is adequate justification for an attempt to find reliable means for eliminating any abnormal susceptibility to corrosive attack.

The most obvious method for rendering all metal surfaces free of extraneous chemicals and/or "abnormal" metal is to subject them to chemical cleaning. Such steps might include alkaline degreasing, followed by pickling or etching in a suitable acid solution. These treatments are more or less conventional in the final finishing of stainless steel for chemical processing equipment, piping, reaction vessels, and similar apparatus. The chemicals required are extremely active, however, requiring very close control of temperature, concentration, and treatment time--not to mention the need for scrupulously thorough rinsing after treatment.

The sizes and shapes of the ducts required in space booster vehicles are such that a similar approach here is not inviting. Not only would extremely large processing tanks be required, but the complexity of the components themselves makes adequate removal of the cleaning agents a questionable task.

The investigation reported here was undertaken for the purpose of developing a cleaning technique which would accomplish the objectives discussed above, but which would not introduce the hazards associated with conventional cleaning and pickling. More specifically, the objective was to develop a technique in which a jet of solution could be directed onto the surface of the metal to be treated, and a current passed in such a way as to "electropolish" or "electroclean" the surface.

Such a method has been developed. The principles involved in electrolytic jet cleaning are described first, followed by an account of the experimental work. The results are then presented, together with the conclusions reached and suggestions for practical utilization of the method.

II. THEORY OF ELECTROLYTIC JET CLEANING

When two metallic electrodes are placed in an electrolyte and a direct current is passed between them, an oxidation reaction is induced at one electrode and a reduction reaction at the other. Oxidation occurs at the "anode"--the terminal connected to the positive side of the DC source--while reduction occurs at the "cathode." The specific reactions which occur at the electrodes, however, are determined by the relative ease of oxidation or reduction of the particular chemical species which are present at the electrode-electrolyte interfaces.

In general, the most easily oxidized substance is consumed at the anode, while the converse is true at the cathode. Sometimes more than one reaction occurs at one or both of the electrodes, the relative proportion being determined by the concentrations and mobilities of the various reactants, as well as by their ease of oxidation or reduction.

The electrode reactions in some instances involve only materials in the solution, the electrodes themselves being inert. This type of reaction occurs, for example, when platinum electrodes are used to pass current through a salt solution. The oxidation product (at the anode) is oxygen, while the reduction product (at the cathode) is hydrogen.

Quite another kind of reaction occurs, however, when the electrodes are not inert. The metal which constitutes the anode may itself be oxidized. This is the effect sought in the present work. The objective is to find electrolytic solutions in which the metals of interest will undergo smooth anodic dissolution when subjected to electrolytic treatment.

There are several forms which anodic attack may take, depending upon the particular metal, the electrolyte, and the other parameters of the cell system. The oxidation product of the metal may be an insoluble coating of oxide which covers the surface, rendering further oxidation difficult; it may be a very soluble ionic product which readily diffuses away into the solution, permitting continued, steady attack on the metal. Of even more concern is the fact that the distribution of oxidation intensity may be either very uniform, leaving a smooth surface, or it may be spotty

and irregular, producing severe pitting. Obviously, the objective of the present study is to produce uniform metal removal, leaving a smooth surface--hopefully even smoother than before treatment.

Finally, it should be noted that the "driving force" toward oxidation of the metal anode in an electrolytic solution is virtually unlimited, being directly proportional to the voltage which is caused to appear at the anode/solution interface. The practical significance of this fact is that the electrolytic solution need not be "active" or "corrosive" in its own right. It derives its ability to dissolve the metal surface from the applied EMF, and the reaction may therefore be readily controlled. Oxidizing power equivalent to strong nitric acid or to elemental chlorine may, for example, readily be generated in electrolytic solutions as innocuous as sodium nitrate, sodium chloride, or phosphoric acid.

III. EXPERIMENTAL WORK

A. Apparatus

In order that a wide variety of electrolytes might be investigated in the same experimental device, materials were selected carefully. A large Monel tray was constructed, having a central drain and a 2 in. lip around the edges. It was supported on a wooden frame, as shown in Figure 1.

A plastic cover was assembled from 0.125 in. Lucite sheet, and provided with an access port in the center of one side. The bottom was open, permitting ready drainage of electrolyte to the sump at the center of the tray. The arm-port could be fitted with a large rubber glove when required for the particular electrolyte under investigation.

This arrangement was very convenient, since the Lucite splash cover could be lifted quickly to the opposite end of the tray when specimens were inserted or removed from the tray.

The electrical circuit is shown schematically in Figure 2. Contact between the workpiece and the tray was made automatically, since the



FIG. 1 - JET ELECTROCLEANING APPARATUS.

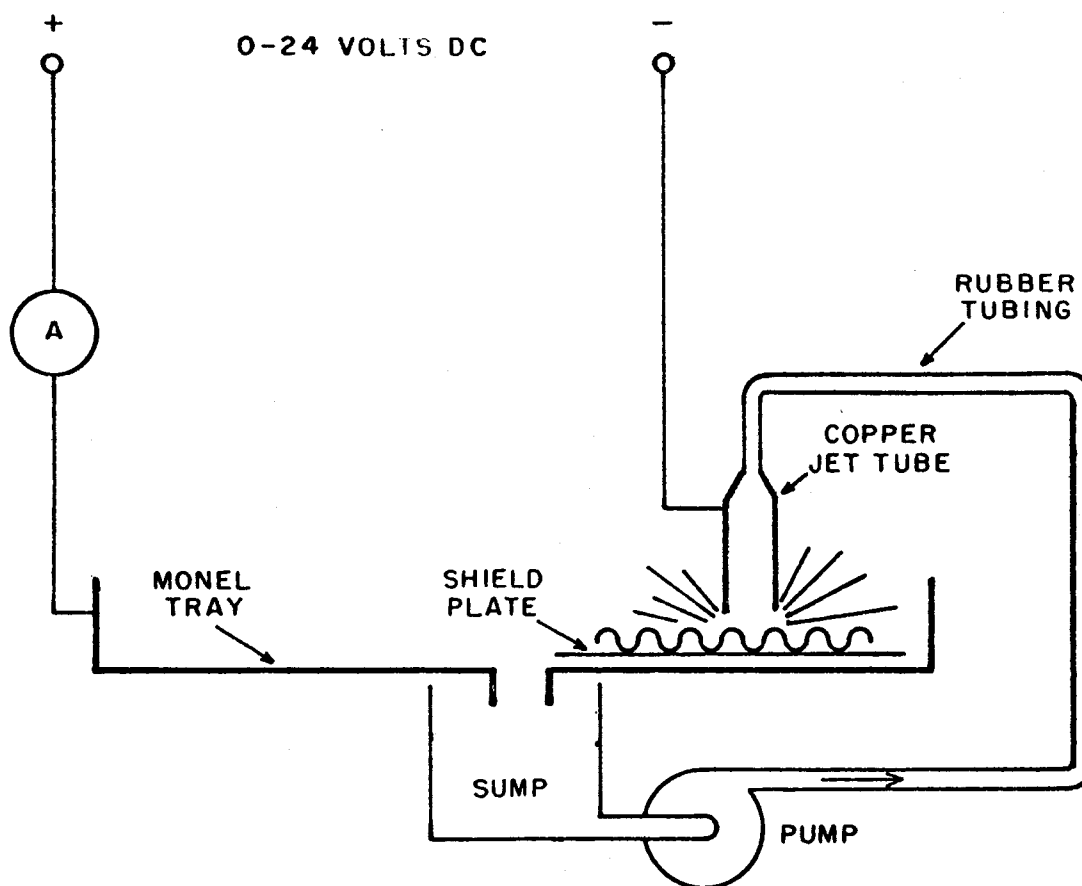


FIG. 2 - SCHEMATIC DIAGRAM OF JET ELECTROCLEANING DEVICE

tray was connected externally to the positive side of the DC source. The shield plate was used to prevent excessive attack on the Monel tray during repeated runs.

When hot solutions were used as electrolytes, the collecting vessel under the Monel tray was placed on a large hot plate, permitting ready control of the electrolyte temperature.

The circulating pump was a 10 gpm stainless steel pump, connected to the jet nozzle with flexible rubber tubing. The pressures involved were only a few psi, since no restriction to flow was incurred by the nozzle design adopted.

In the early tests, the nozzle was a short section of 3/8 in. copper tubing. In later experiments, it was increased to 1 in. diameter, with much greater current flow resulting. Several other variations were studied, including a "flattened-tube" configuration, a tubular nozzle fitted with a perforated plate, and a "brush-tipped" nozzle. The several types of electrodes studied are shown in Figure 3.

After many experiments, it was concluded that the best design was the simple, large diameter tube, fitted with a nonshorting tip. This nozzle gave the largest cross-section of electrolyte between the work and the jet tube, and therefore produced the highest cleaning current. Since the metal removal rate is proportional to the current, this obviously results in the fastest cleaning of a given area.

It was originally hoped that current densities on the order of those attainable in electrolytic machining might be reached here also. This was not feasible, however, since the dimensions of the electrolytic path are necessarily much longer than those met in electrolytic machining. The current, therefore, is limited by the electrolyte resistance, and no degree of agitation, flow velocity, or other change in the conditions existing at the electrodes will appreciably increase the current. It is possible, of course, to increase the current by raising the applied voltage. The use of voltages in excess of 25 volts, however, is hazardous to the operator and was not given further consideration in the present problem.

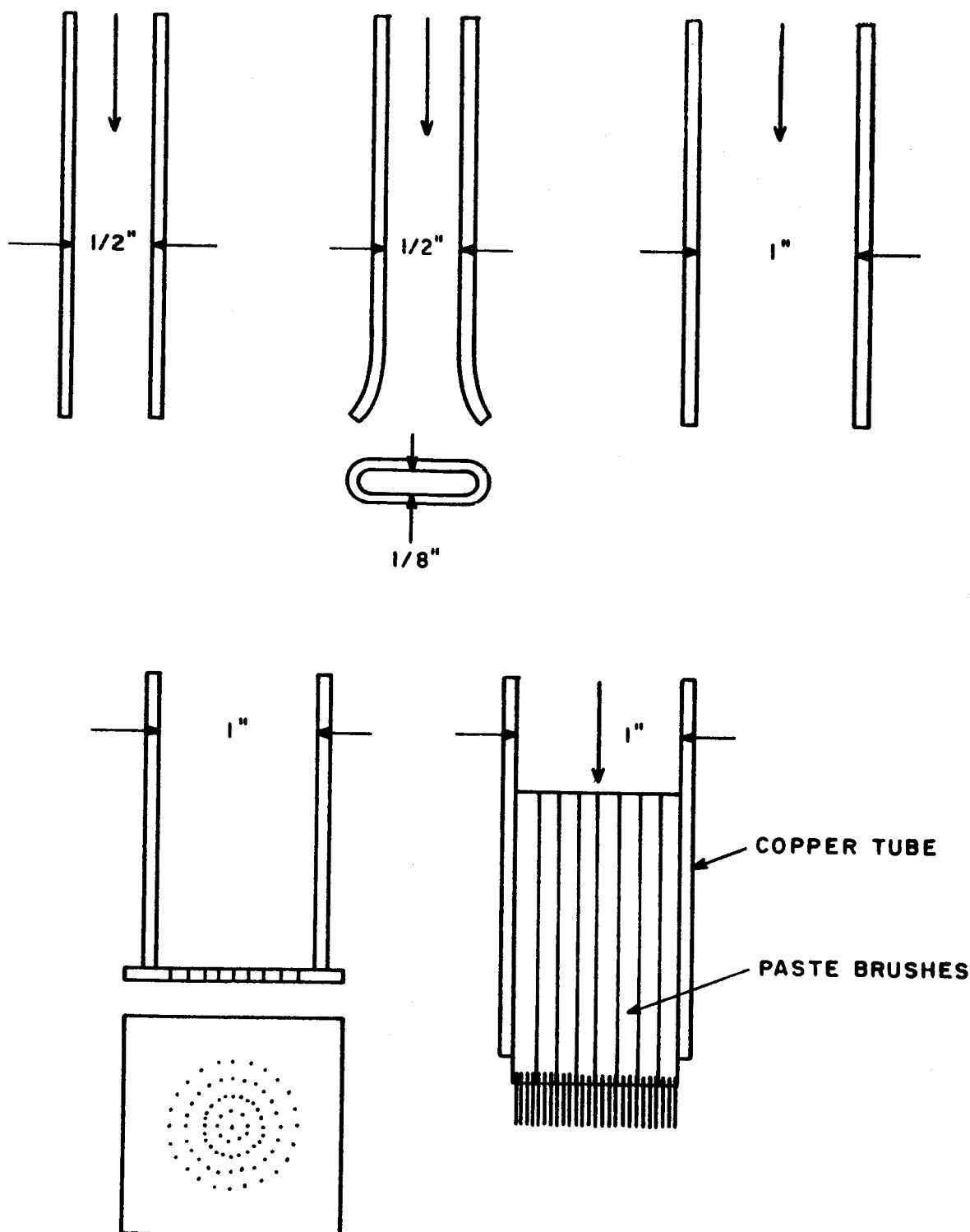


FIG. 3 - NOZZLE CONFIGURATIONS

B. Materials

The metals from which flexible components of fuel and oxygen lines may be constructed include:

1. Type 321 stainless steel
2. A-286
3. Inconel 718
4. Hastelloy C
5. René 41

Specimens of each of these alloys were obtained in the form of actual finished hardware. They were cut into smaller sections for electropolishing experiments with various electrolytes.

Prior to performing electrocleaning tests, the several materials were (in most cases) subjected to oxidation by heating in air. This was done in the belief that a successful cleaning method must be capable of removing rather severe oxide coatings (from regions in the vicinity of welds, for example). Actually, of course, the degree of oxidation to which any of these alloys is subjected during fabrication is very slight. At most, a trace of interference color is visible at weld zones, the balance of the surface being extremely free of oxide. Accordingly, later experiments employed as-fabricated components; the electrocleaning treatment was used merely to remove the outer "skin" of the metal.

Although the conditions selected for evaluation of various electrolytes were very demanding, they nevertheless permitted quite critical distinctions to be made among the experimental baths. Had all experiments been done on unoxidized specimens, it would have been difficult to rate the metal-removal power of each, or to judge the "throwing power" of the electrolytic action on convoluted surfaces.

C. Electrolyte Survey

1. Choice of Electrolytes

When the concept of jet electropolishing was first considered, it was anticipated that the selection of electrolytes would most probably be made from conventional solution compositions that are used in metal finishing operations, metallographic procedures, and similar metal "brightening"

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processes. These are primarily combinations of one or more of the acids: chromic, sulfuric, and phosphoric. Such solutions are customarily used at elevated temperature and are usually not stirred vigorously during polishing.

The theory of operation of these baths--while certainly not completely established--is generally believed to be that a viscous film forms in the immediate vicinity of the work surface, through which metal dissolution takes place. "High" spots are thought to be attacked more rapidly than "low" spots because they more or less "protrude" through this viscous film.

It is at once evident that direct adoption of such electropolishing baths for use where vigorous agitation will be involved and where very high temperatures would be inconvenient, may not be practical. Furthermore--and this disadvantage became more evident as the experimental work progressed--the extremely noxious character of strong acid mixtures, especially when hot, makes their use in a large-scale jet apparatus rather uninviting.

When the basic objectives of the proposed jet electrocleaning technique were reviewed critically, it was realized that the need was not specifically for a brightening or polishing action, so much as it was for a "metal-removal" technique. Of course, such a method should produce a satisfactorily smooth surface--and polishing would be welcome--but it need not be obtained at the sacrifice of convenience, safety, or economy of operation.

Immediate consideration was given, therefore, to non-toxic, non-hazardous, inexpensive solutions which could be used at room temperature (or slightly above). Experience with electrochemical milling had already demonstrated that surprisingly smooth surfaces can be achieved even with simple salts such as sodium chloride.

2. Degree of Metal Contamination

Preliminary experiments were run using 10% sodium chloride solution as the electrolyte and flat sheet specimens of Type 304 stainless

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steel as workpieces. The stainless steel was oxidized in air at various temperatures to produce a controlled oxide coating. Samples were heated at 300°, 600°, 1000°, 1300°, and 1600° F.

The degree of oxidation produced at 300° or 600° F was too slight to produce much contrast with the clean metal surface. The oxide film produced at 1000° F was moderate, and turned out to be a reasonable test surface for electrolytic cleaning experiments. The oxides produced at 1300° and 1600° F were too heavy to be removed without excessive loss of base metal.

Figure 4 shows coupons of Type 304 stainless steel, preoxidized at 1000° F for one hour, and electrolytically cleaned on their lower halves. When only a very thin oxide film was present, cleaning was extremely rapid; where locally thicker films were present (right hand specimen), cleaning was slower.

In further work on the other alloys, the degree of oxidation was arbitrarily selected to represent the amount which might reasonably be expected if inadvertent atmosphere contamination occurred during heat treatment or welding of the material.

IV. RESULTS

In Table I are shown the conditions used and the results obtained in a series of electrolyte variations. The type of cleaning obtained with each of the alloys is illustrated in Figures 5, 6, and 7. In general, A-286 and Type 321 stainless steel were most readily cleaned. The oxide films on the other alloys were more adherent, generally requiring at least a modest degree of mechanical scrubbing action to dislodge all traces of the oxide.

When only thin oxide films--or none at all--are present, removal of the outermost metal surface is readily accomplished, leaving a satin finish.

Similarly, when the metal surface has no convolutions, it is readily cleaned, even when fairly heavy oxides are present. This is

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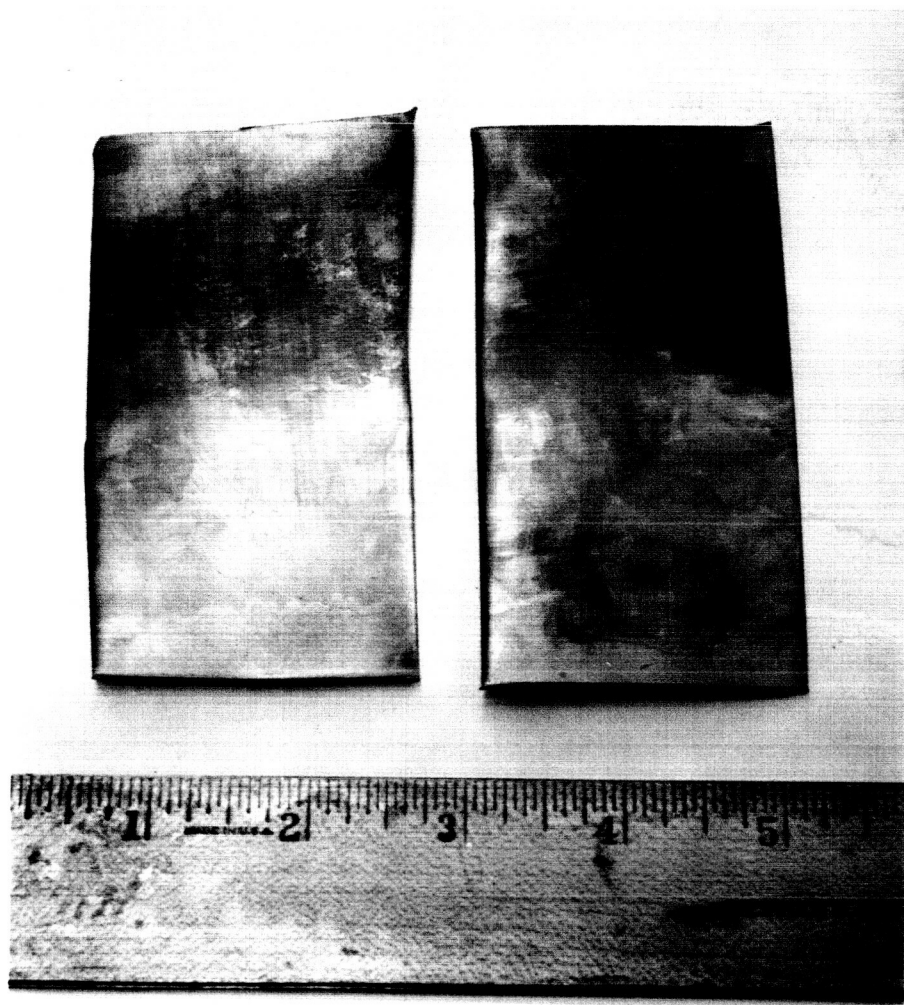


FIG. 4 - CLEANING OF 18-8 STAINLESS
STEEL.

TABLE I
ELECTROLYTIC CLEANING EXPERIMENTS

Applied voltage: 22-23 volts
Samples preoxidized by heating in air

Run No.	Solution	Temp.	Nozzle*	Max. Current, amps	Material	Cleaning Action
1	10% sodium chloride	Room	3/8-in. round	1	18-8SS	Slow cleaning
2	10% sodium chloride	Room	Fishtail	<1	18-8SS	Slow cleaning
3	10% sodium chloride	Room	1-in. round	14	18-8SS	Good cleaning (1 minute)
4	5% citric acid	Room	1-in. round	6	18-8SS	Not as good as 10% NaCl
5	20% sodium chloride, 5% sodium gluconate	Room	1-in. round	3	18-8SS	Loosens heavy oxide, but does not remove completely
6	20% sodium chloride, 5% sodium gluconate, 3% suspended feldspar	Room	1-in. round	3	18-8SS	Clean, but etched
7	20% sodium chloride, 5% sodium gluconate, 3% suspended feldspar	Room	Brush-tipped electrode	3	18-8SS	Cleans well; no etching
8	50% phosphoric acid, 50% sulfuric acid	100°C and Room	(Beaker-scale tests)		Hastelloy-C Type 321SS A-286 Inconel 718 René 41	Good polishing Good polishing Good polishing Cleaning, but not good polishing Cleaning, but not good polishing

TABLE I (Cont'd.)

Run No.	Solution	Temp.	Nozzle*	Max. Current, amps	Material	Cleaning Action
9	57.5% phosphoric acid, Room 20% sulfuric acid, 1% chromic acid, balance water	Room	(Beaker-scale tests)		Hastelloy C Type 321 SS A-286 Inconel 718 René 41	Good polishing Good polishing Good polishing Oxide loosened Oxide loosened
10**	20% sodium chloride, Room 5% sodium gluconate	Room	1-in. round	6	Inconel 718	Cleaning fair to good. Some spots left; bottoms of convolution slightly cleaned. Very poor Very poor; cleaning on crests only Good; cleaning on crests and partly into bottoms Good; similar to A-286
11	57.5% phosphoric acid, Room 20% sulfuric acid, 1% chromic acid, balance water	Room	1-in. round	4	Rene 41 Hastelloy C A-286 Type 321 SS Inconel 718 René 41 Hastelloy C A-286 Type 321 SS	No true cleaning; oxide dislodged, but not re- moved. Oxide loosened, but not removed. Oxide loosened, but not removed. Cleaning on high points only; valleys not cleaned. Oxide loosened, but not removed.

TABLE I (Cont'd.)

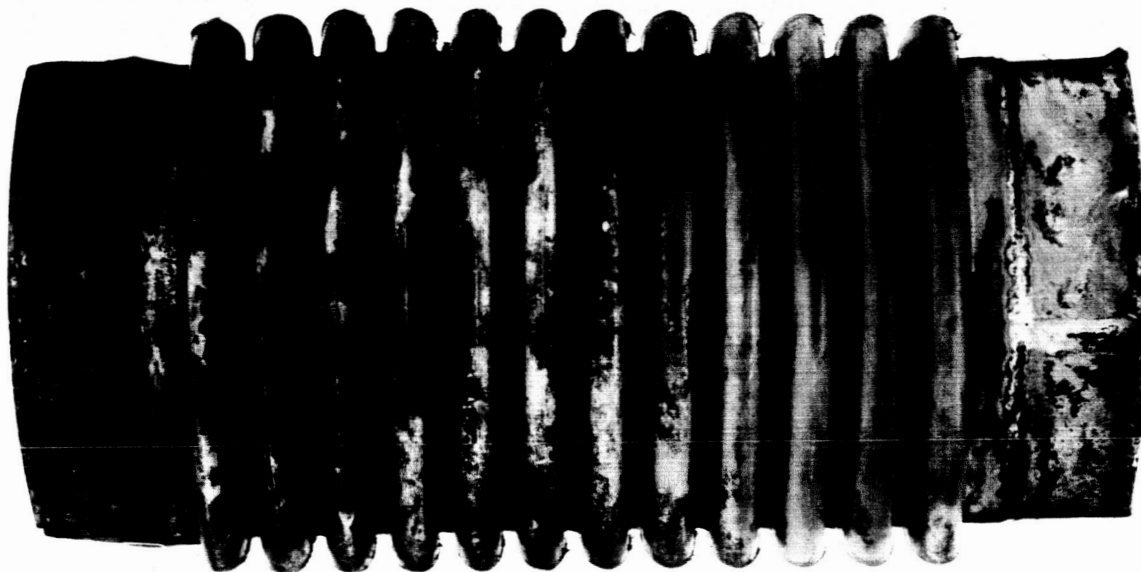
Run No.	Solution	Temp.	Nozzle *	Max. Current, amps	Material	Cleaning Action
12	10% sodium nitrate	Room	(Beaker-scale tests)		Inconel 718 Rene 41 Hastelloy C A-286 Type 321 SS	Smut formation on all alloys
13	10% sodium fluoborate	Room	(Beaker-scale tests)		Inconel 718 Rene 41 Hastelloy C A-286 Type 321 SS	Smut formation on all alloys
14	10% sodium nitrate	Room	1-in. round	2	Inconel 718 Rene 41 Hastelloy C A-286 Type 321 SS	Smut formation; poor cleaning on all alloys
15	20% sodium nitrate	Room	1-in. round	4	Inconel 718 Rene 41 Hastelloy C Type 321 SS A-286	No cleaning; smut. No cleaning; smut. No cleaning; smut. No cleaning; smut. Good cleaning.
16	20% sodium chloride, 5% sodium gluconate	Room	"Shower head"	4	Inconel 718 Rene 41 Hastelloy C Type 321 SS A-286	Cleaning slow; smut. Cleaning slow; smut. Cleaning slow; smut. Cleaning slow; smut. Fairly good cleaning.

TABLE I (Cont'd.)

Run No.	Solution	Temp.	Nozzle *	Max. Current, amps	Material	Cleaning Action
17	30% sodium chloride, 5% sodium gluconate	120°F (49°C)	"Shower head"	1	Inconel 718 Rene 41 Hastelloy C Type 321 SS A-286	Poor cleaning on all alloys
18	30% sodium chloride, 5% sodium gluconate	120°F (49°C)	1-in. round with rubber sleeve at tip	25	A-286 Inconel 718 Rene 41 Hastelloy C Type 321 SS	Good cleaning on high spots No cleaning; smut No cleaning, smut Fair cleaning on high spots Fair cleaning on high spots
19	30% sodium chloride, 5% sodium gluconate	120°F (49°C)	1-in. round with rubber sleeve	25	Type 304 SS (in form of smooth cylin- der)	Excellent cleaning
20	30% sodium chloride, 5% sodium gluconate	120°F (49°C)	1-in. round with rubber sleeve	5	Hastelloy C (unoxidized) Type 321 SS (unoxidized)	Smooth satin finish Smooth satin finish

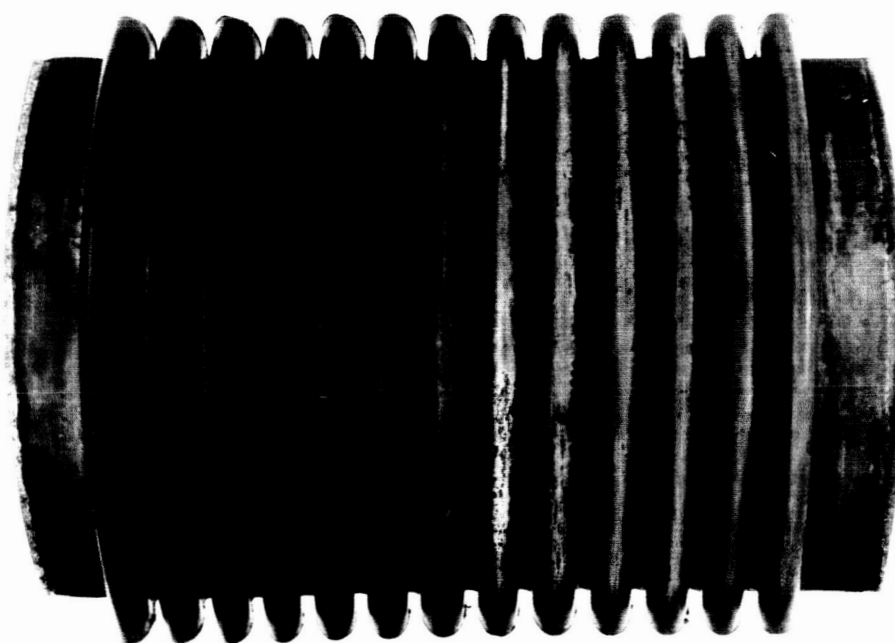
* See Figure 3

** See Figures 5, 6, and 7



Neg. No. 26177

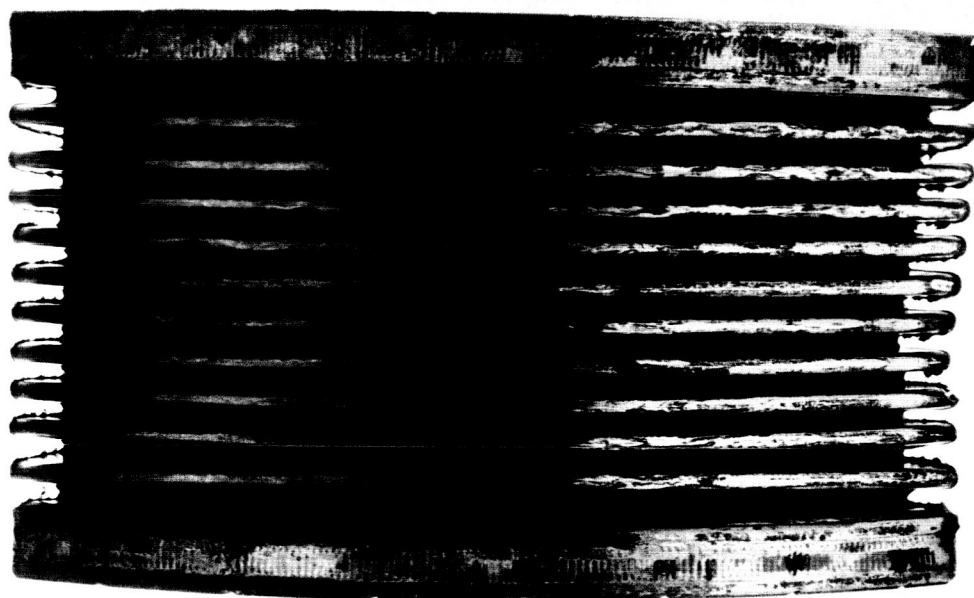
(a) Inco 718



Neg. No. 26180

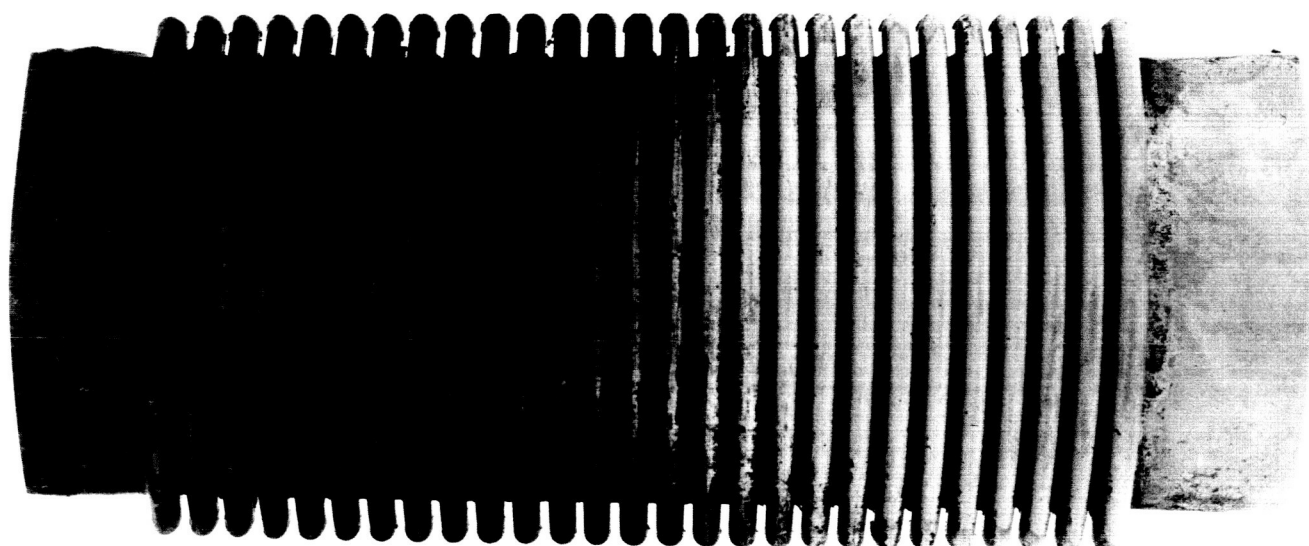
(b) René 41

FIG. 5 - ELECTROLYTIC CLEANING OF METAL BELLOWS.
(See Run No. 10, Table I).



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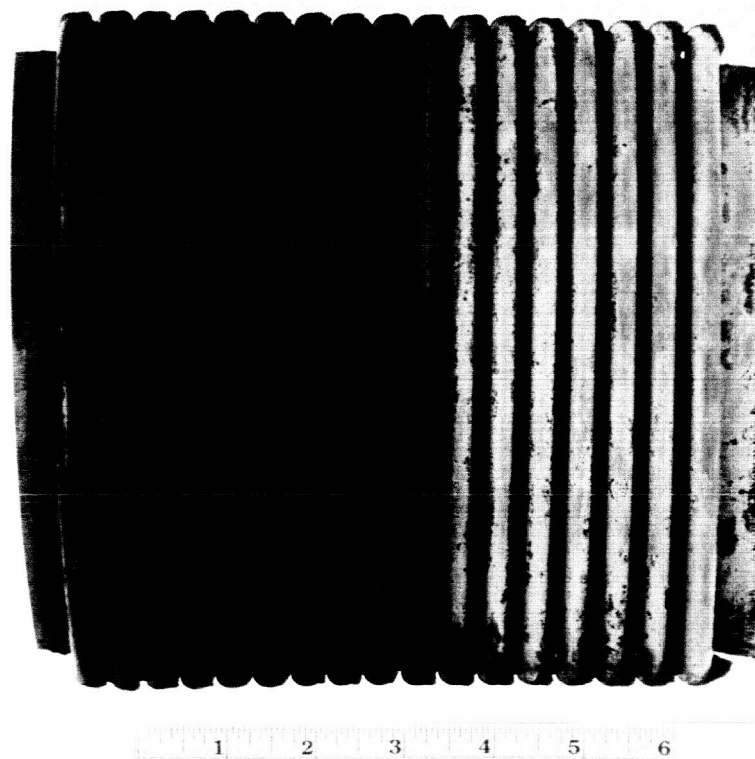
(a) Hastelloy C



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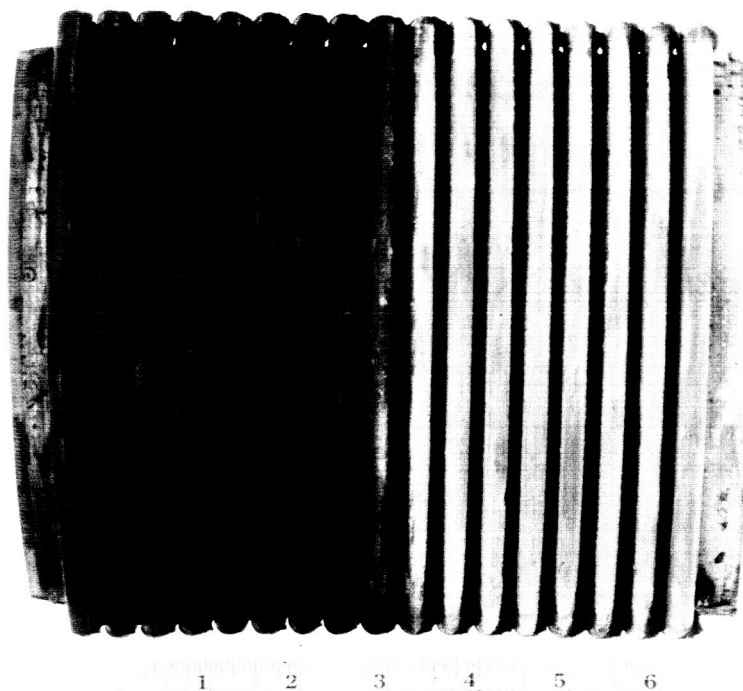
(b) A-286

FIG. 6 - ELECTROLYTIC CLEANING OF METAL BELLOWS.
(See Run No. 10, Table I)



Neg. No. 26181

(a) Type 321-SS



Neg. No. 26179

(b) Duplicate Specimen of Type 321-SS

FIG. 7 - ELECTROLYTIC CLEANING OF METAL BELLOWS.
(See Run No. 10, Table I)

illustrated in Figure 8, where the interior surface of a Type 304 stainless steel cylinder was electrocleaned in 30% sodium chloride, 5% sodium gluconate, at 120°F. No mechanical scrubbing was used; the electrolyte jet was sufficient to remove oxide fragments as they were loosened.

Samples of both Hastelloy C and Type 321 stainless steel were jet-electrocleaned, using the 30% sodium chloride, 5% sodium gluconate solution (Run 20, Table I). In each of these experiments, the electrolytic treatment was applied solely for the purpose of removing the outermost layer of metal (no preoxidation of the surface was used). The objective was to determine the effect of such surface removal on subsequent corrosion in a salt spray exposure.

Unfortunately, the control samples of each of the two metals did not suffer any significant corrosion when exposed to 1000 hours of salt spray testing (conducted in accordance with specification MIL-E-5272A). The surface-treated specimens likewise suffered no noticeable attack, making judgment concerning the efficacy of the electrocleaning treatment impossible.

It should be emphasized, however, that the appearance of the alloys after electrolytic treatment was not greatly different from that of the original samples, the major effect being one of "homogenizing" the surface to a rather uniform "satin" finish.

V. CONCLUSIONS

The jet-impingement technique is well adapted to the removal of the surface layer from finished parts such as flexible metal ducts. It has been found that such surface cleaning can be accomplished with very mild electrolytes; the usual acid electropolishing solutions, in fact, do not product as satisfactory surface finish under jet-impingement conditions as does a simple salt solution.

One of the most satisfactory solutions for electrolytic cleaning of stainless steel is 30% sodium chloride, 5% sodium gluconate. Essentially equal results are obtained from 20% sodium chloride, 5% sodium

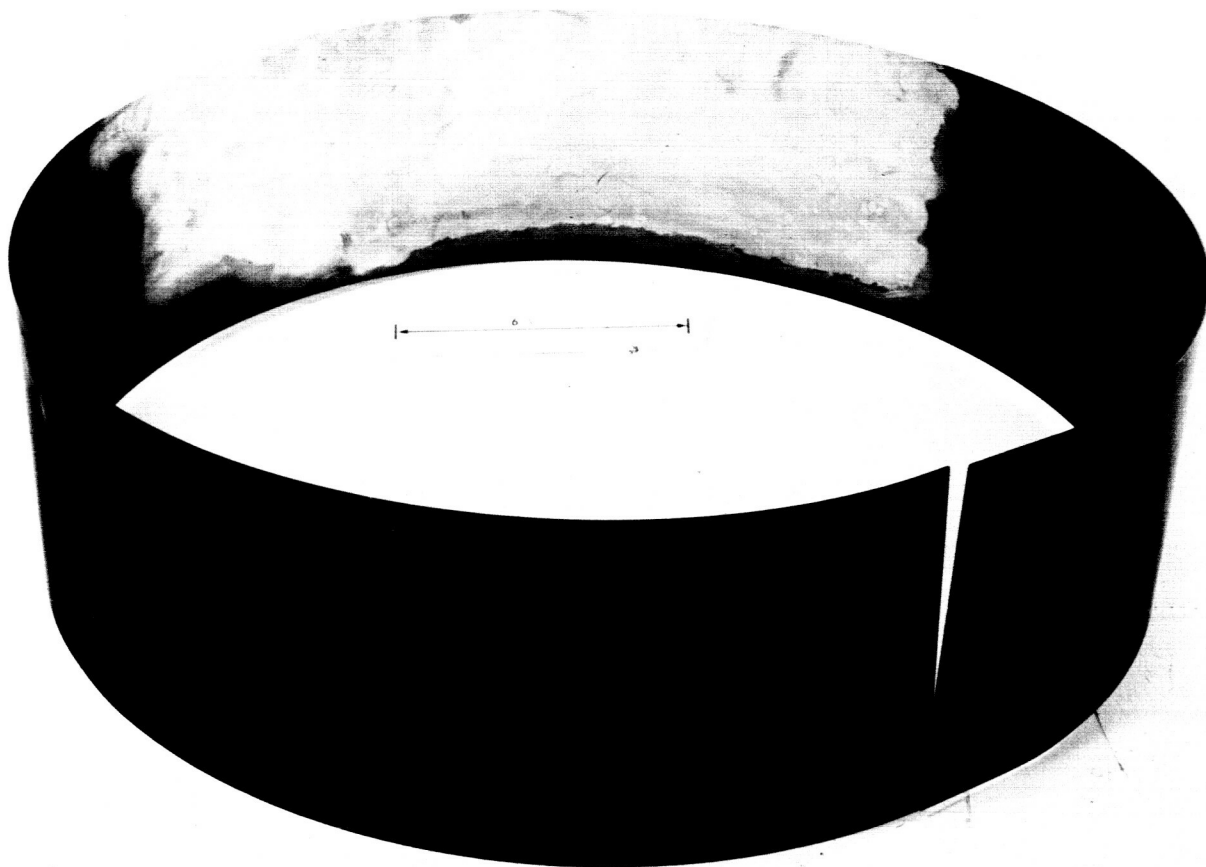


FIG. 8 - ELECTROLYTIC CLEANING OF SMOOTH TYPE 304 STAINLESS STEEL. (See Run No. 19, Table I)

gluconate, the former being somewhat more conductive. The alloys Inco 718 and Rene 41 did not respond well to any of the electrolytes studied when severely oxidized; when essentially oxide-free, however, they are anodically attacked quite readily and yield smooth surfaces.

It is believed that the jet-impingement method can be used to produce a surface essentially equivalent to a "bright-dipped" or otherwise "pickled" surface, without the need for the extremely large tanks which would be required for total immersion of large fabricated components.

Furthermore, the discovery that metal removal can be effected in a controlled manner--using nontoxic, inexpensive, and easily removed chemicals--will make it possible to work with conventional equipment for handling the electrolyte in nonhooded areas, and with unprotected personnel.

The fact that reasonable currents can be passed with DC voltages in the range of 20-25 volts means that no electrical hazard to personnel is introduced. While it is desirable to use the sodium chloride electrolyte at a somewhat elevated temperature (120°F) for more rapid metal removal, essentially equivalent surface appearance is achieved with the solution at room temperature.

VI. LOGBOOKS AND CONTRIBUTING PERSONNEL

Data used in preparation of this report are recorded in IITRI Logbook No. C-14243.

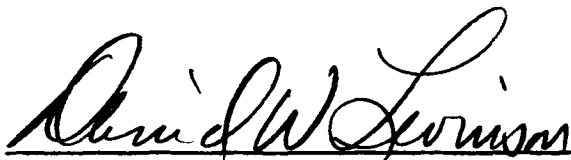
Personnel contributing to the execution of the experimental work include J. C. Kaminski and H. T. Francis.

The cooperation of Flexonics Division of Calumet and Hecla and of Arrowhead Products Division of Federal-Mogul-Bower Bearings, Inc. in providing specimens of the several alloys in fabricated form is acknowledged with thanks.

Respectfully submitted,
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